

PATENT ABSTRACTS OF JAPAN

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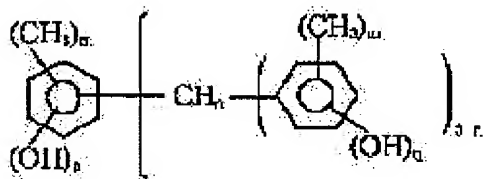
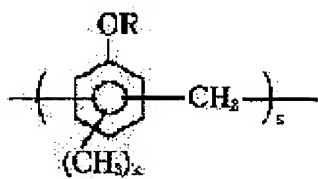
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(54) POSITIVE TYPE RESIST COMPOSITION



(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a positive type resist material excellent in a uniformity, having a high sensitivity and a high resolution and excellent also in a heat

I resistance and a property of a film endurance by using novolak resin having properties of both an alkali-soluble resin and a sensitizer and a dissolution accelerator having phenolic hydroxyl groups as an essential components.

SOLUTION: This positive type resist compsn.

contains a resin having repeating units

represented by formed I and a wt. average

II mol.wt. of 1,000-10,000, a dissolution

accelerator having phenolic hydroxyl groups

represented by formula II and a solvent dissolving them. The amt. of the dissolution accelerator is 0.5-10 pts.wt. per 100 pts.wt. of the resin. In the formula I, 2-27% of R's are a residue of 1,2-naphthoquinonediazido-4-sulfonic ester and/or a residue of 1,2-naphthoquinonediazido-5-sulfonic ester, the remainders are H, (K) is an integer of 0-3 and (s) is a number satisfying the wt. average mol.wt. In the formula II, each of (m) and (p) is an integer of 0-3, (n) is 1 or 2, (q) is an integer of 1-3 and (r) is 1 or 2.

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CLAIMS

[Claim(s)]

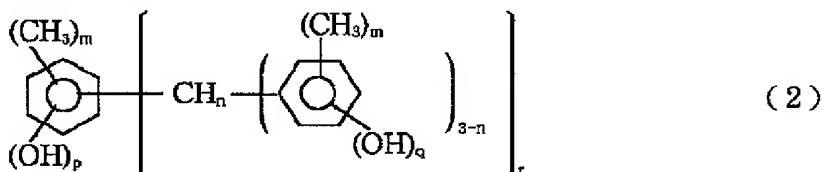
[Claim 1] The positive-resist constituent which contains the dissolution accelerator which has the phenolic hydroxyl group shown by the following general formula (2) at a rate of 0.5 – 10 weight section to the resin 100 weight section of weight average molecular weight 1,000–10,000 which has the repeat unit shown with the general following structure expression (1), and comes to contain the solvent which dissolves these further.

[Formula 1]



(Among a formula, the 2-27-mol % is 1 and 2-naphthoquinonediazide-4-sulfonate residue and/or 1, and 2-naphthoquinonediazide-5-sulfonate residue, and the remainder of R is a hydrogen atom.) It is the number with which k fulfills the integer of 0–3 and s fulfills the above-mentioned weight average molecular weight.

[Formula 2]



(For m and p, the integer of 0-3 and n are [1-3r of 1 or 2, and q] the integers of 1 or 2 among a formula, respectively.)

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the positive-resist constituent of the novolak system which gives the resist film which was excellent in high resolution at thermal resistance and residual membrane nature.

[0002]

[Description of the Prior Art] Conventionally, the novolak system resist constituent has been prepared considering two components of novolak resin and a sensitization agent as a principal component. However, in order to obtain the resist constituent which was more excellent in high resolution at thermal resistance and residual membrane nature, and suited the wavelength of the light source of various exposure machines, much devices have been made from the field of both novolak resin and a sensitization agent. If an example is given from the field of novolak resin, and the mean molecular weight of the novolak resin to compound becomes small, while the resolution as a resist improves, it will become a thing inferior to thermal resistance and residual membrane nature (BREAK THROUGH, the February, 1992 issue, 18 pages). Therefore, the technique of removing low-molecular-weight novolak resin is proposed by processing of the reprecipitating method etc. in compound novolak resin. Moreover, by the benzophenone system sensitization agent used conventionally, if an example is given from the field of a sensitization agent, when the light source of an exposure machine changes from g line to i line, since light is hard coming to penetrate the inside of the resist film, the proposal of using the sensitization agent of fewer non-benzophenone systems of absorption by i line has been made (a Nikkei micro device, the April, 1992 issue, 45 pages).

[0003] However, in order to combine such technique and to realize the resist constituent of high resolution more, in the production process of a resist constituent, it was needed like much additional processing, and there was disadvantage, such as leading to the cause of a cost rise.

[0004] This invention was made in order to improve the above-mentioned situation,

and it aims at offering the positive-resist constituent of the novolak system which gives the resist film which is high resolution and was excellent in thermal resistance and residual membrane nature.

[0005]

[The means for solving a technical problem and the gestalt of implementation of invention] In alkali fusibility resin, such as cresol which has the repeat unit shown with the general following structure expression (1) as a result of inquiring wholeheartedly, in order that this invention persons may attain the above-mentioned object, or xylene novolak resin 1 and 2-naphthoquinonediazide-4 or the resin 100 weight section of weight average molecular weight 1,000-10,000 formed into 5-sulfonate is received selectively. The constituent which blended the dissolution accelerator which has the phenolic hydroxyl group shown by the following general formula (2) in the range of 0.5 - 10 weight section carries out the knowledge of giving the resist coat which was excellent in homogeneity and was excellent in high sensitivity and high resolution at thermal resistance and residual membrane nature, and it comes to make this invention.

[0006]

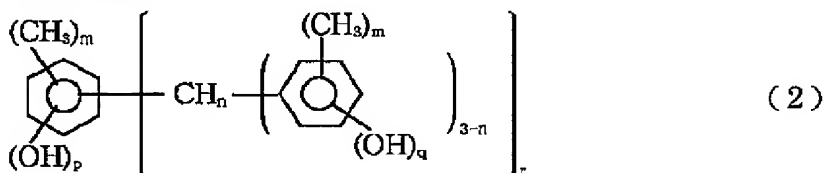
[Formula 3]



(Among a formula, the 2-27-mol % is 1 and 2-naphthoquinonediazide-4-sulfonate residue and/or 1, and 2-naphthoquinonediazide-5-sulfonate residue, and the remainder of R is a hydrogen atom.) It is the number with which k fulfills the integer of 0-3 and s fulfills the above-mentioned weight average molecular weight.

[0007]

[Formula 4]



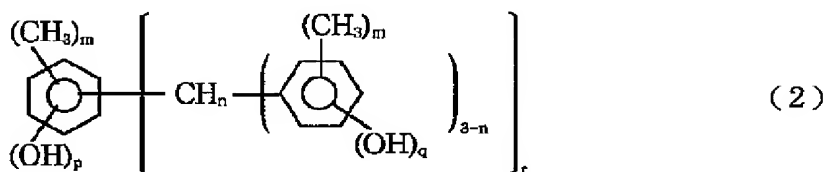
(For m and p, the integer of 0-3 and n are [1-3r of 1 or 2, and q] the integers of 1 or 2 among a formula, respectively.)

[0008] Hereafter, lessons is taken from this invention and it explains in more detail.

[0009] The positive-resist constituent of this invention contains the dissolution accelerator which has the phenolic hydroxyl group shown by the following general formula (2) at a rate of 0.5 – 10 weight section to the resin 100 weight section of weight average molecular weight 1,000–10,000 which has the repeat unit shown with the general following structure expression (1), and comes to contain the solvent which dissolves these further.

[0010]

[Formula 5]



[0011] Here, among a formula (1), R is hydrogen atom, 1, and 2-naphthoquinonediazide –4 or 5-sulfonate residue, and the rate of sulfonate residue is 3 – ten-mol the number with which it is %, and k fulfills the integer of 0–3 and s fulfills the above-mentioned weight average molecular weight more preferably 2 – 27-mol%. When the rate of esterification is less than [2 mol %], the lysis inhibition effectiveness over the alkali developer of a pattern unexposed part is not enough, when a positive type pattern is not obtained and it exceeds 27-mol %, the solubility over the alkali water solution of the exposure section is not enough, and definition is inferior.

[0012] moreover, the weight average molecular weight of this resin -- 1,000–10,000 -- it is 2,000–8,000 more preferably, and by less than 1,000, when thermal resistance exceeds 10,000 rather than is [and] enough, it is inferior to the definition at the time of pattern formation, and sensibility.

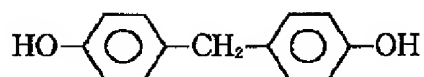
[0013] For m in a formula (2), and p, the integer of 0–3 and n are [1–3r of 1 or 2, and q] the integers of 1 or 2, respectively.

[0014] Specifically, the following are mentioned as a dissolution accelerator which has such a phenolic hydroxyl group.

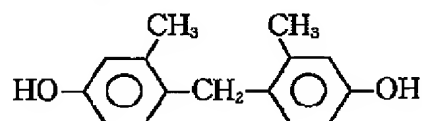
[0015]

[Formula 6]

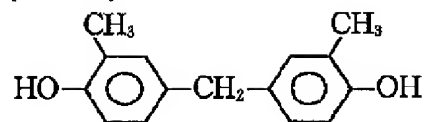
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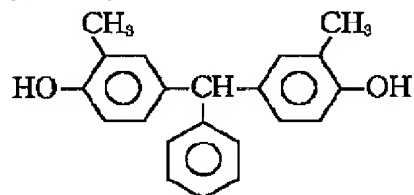
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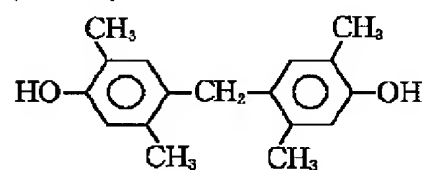
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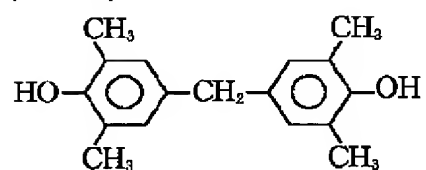
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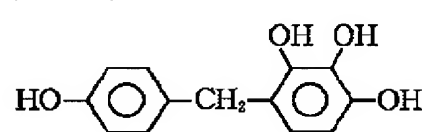
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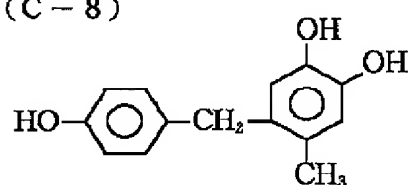
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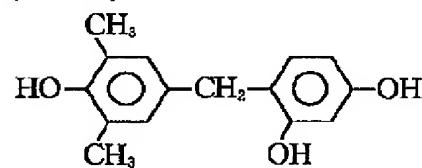
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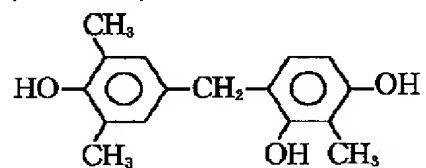
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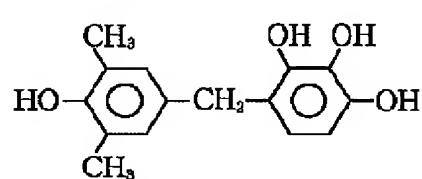
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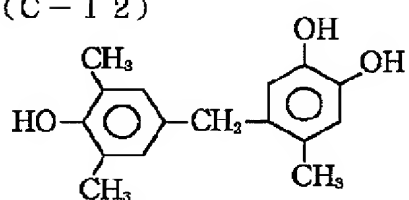
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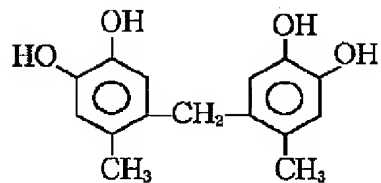
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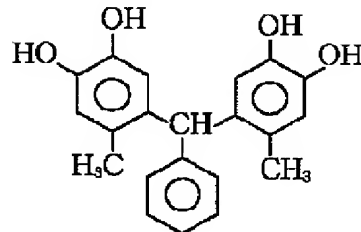
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[Formula 7]

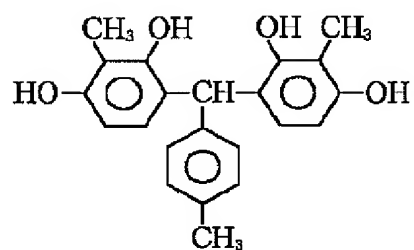
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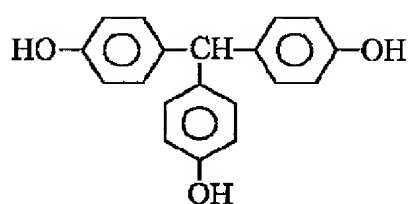
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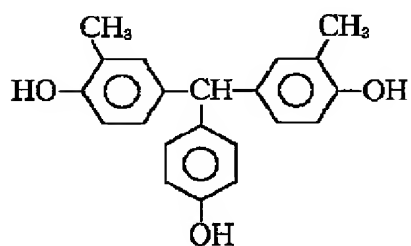
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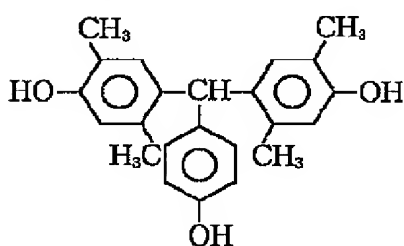
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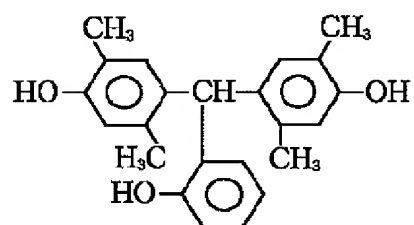
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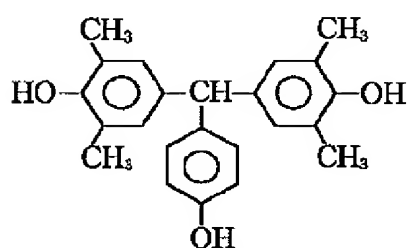
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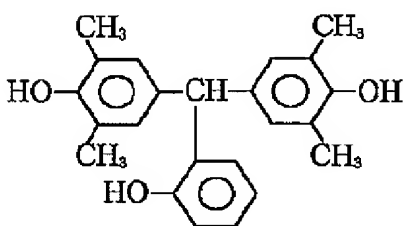
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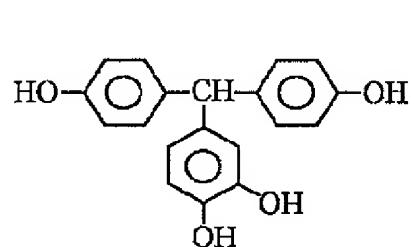
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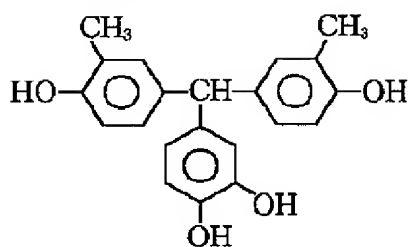
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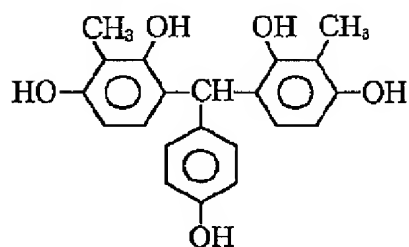
[0017]

[Formula 8]

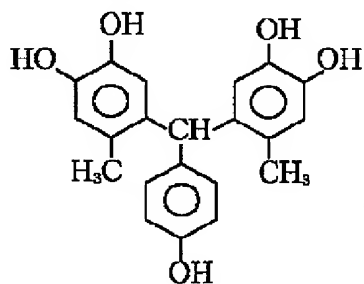
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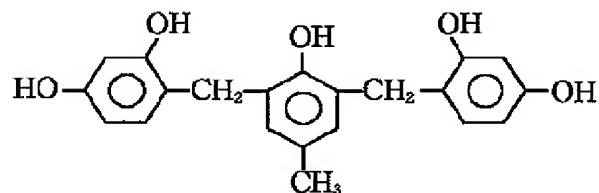
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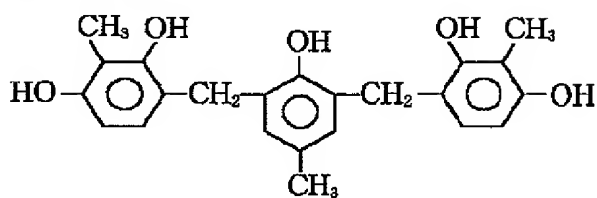
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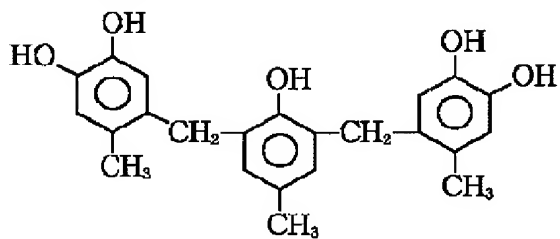
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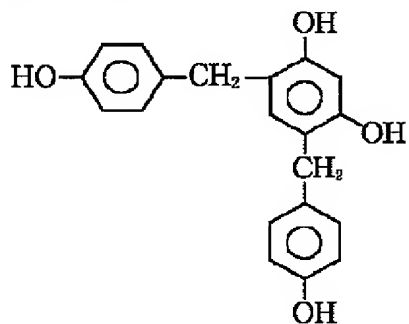
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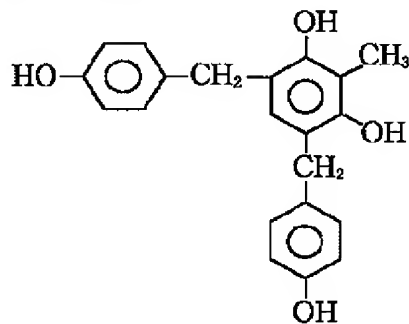
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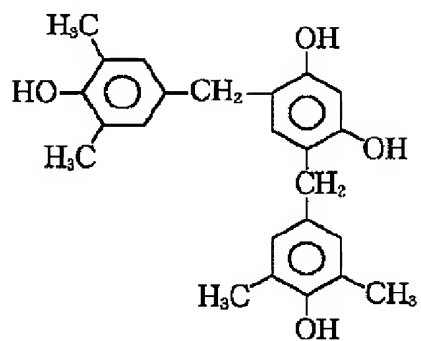
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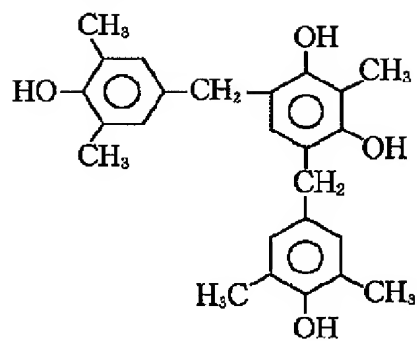
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[Formula 9]

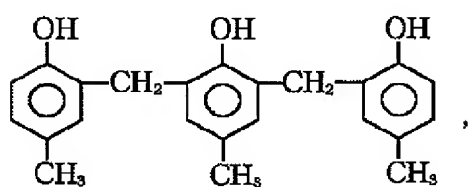
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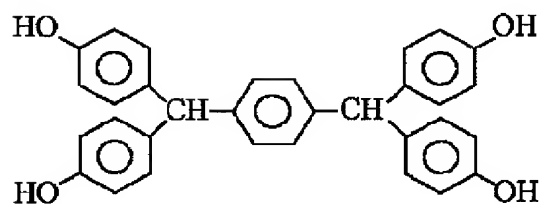
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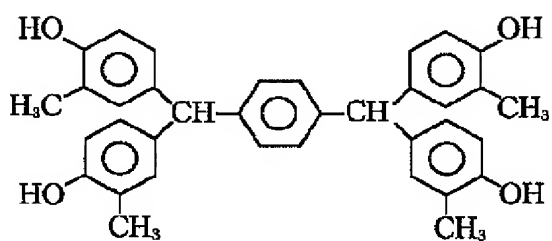
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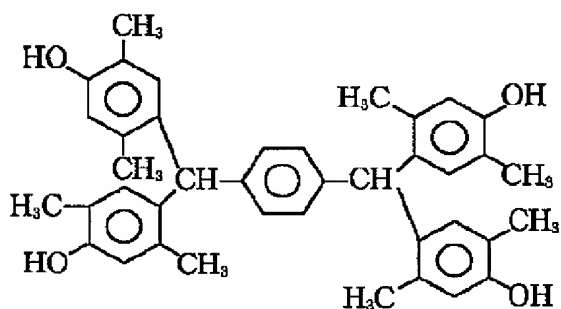
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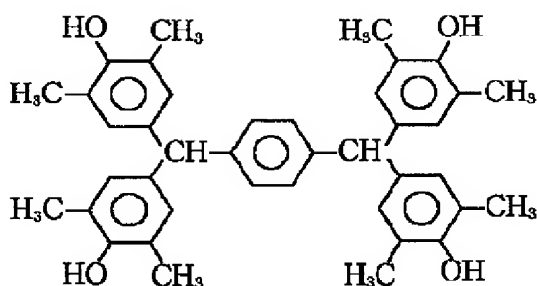
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[0019]

[Formula 10]

(C - 37)



[0020] The addition of the dissolution accelerator which has these phenolic hydroxyl groups needs to be 0.5 - 10 weight section to the resin 100 weight section. In high sensitivity-ization fully being unable to attain when fewer than the 0.5 weight section, and exceeding 10 weight sections, the deformation produced in the resist pattern bottom product section called a micro groove in the pattern configuration after exposure and development takes place, and it is inferior to pattern rectangle nature.

[0021] It dissolves in a suitable solvent and the positive-resist constituent of this invention is obtained so that solid content concentration may serve as 10 - 60 weight section preferably in resin and a dissolution accelerator.

[0022] As a solvent, acetic ester, such as ketones, such as ethylene glycol monoalkyl ether and its acetate, propylene glycol monoalkyl ether and its acetate, diethylene-glycol monochrome or dialkyl ether, lactic-acid alkyl ester, alkoxy propionic-acid alkyl ester, methyl isobutyl ketone, and a cyclohexanone, and butyl acetate, is mentioned, for example. These solvents are independent, or can mix two or more kinds and can be used.

[0023] Moreover, to the constituent of this invention, in order to improve spreading nature if needed, surfactants, such as the Nonion system, a fluorine system, and a silicone system, can be added.

[0024] Especially the usage at the time of forming the resist pattern by radiation irradiation using the positive-resist constituent of this invention is not limited, and can be performed according to the approach of common use.

[0025] For example, on base materials, such as a silicon wafer, the spin coat of the constituent solution of this invention is carried out, and it is prebaked. Then, with aligners, such as a pro squeak tee aligner and a stepper, ultraviolet rays are irradiated and the target resist pattern can be further formed development and by carrying out a rinse. In addition, as a developer, organic alkali water solutions, such as inorganic alkali water solutions, such as a sodium hydroxide and a sodium carbonate, triethanolamine,

tetramethylammonium hydroxide, and a choline, can be used.

[0026]

[Effect of the Invention] The resist constituent of this invention is what used as the principal component the novolak resin which had the engine performance of both alkali fusibility resin and a sensitization agent, and the dissolution accelerator which has a phenolic hydroxyl group, and can be suitably used as a positive-resist ingredient which was excellent in homogeneity, are high sensitivity and high resolution and was excellent in thermal resistance and residual membrane nature.

[0027]

[Example] Although a synthetic example, an example, and the example of a comparison are shown and this invention is explained concretely hereafter, this invention is not restricted to the following example.

[0028] Moreover, in each example, assessment of many engine performance of a resist constituent was performed by the following approach.

(1) It measured by the GPC method by making mono dispersion polystyrene into a criterion using the GPC column (G2000H62 G3000H63 ** [G4000H61]) by the average weight molecular weight Mw Oriental soda company of alkali fusibility resin on analysis conditions with a flow rate tetrahydrofuran [a part for /and the elution solvent tetrahydrofuran of 1.5ml], and a column temperature of 40 degrees C.

(2) After applying the resist constituent prepared on the silicon wafer which carried out the adhesion promoter coat using the spin coater (SKW-636-BV) by the resist thickness great Japan screen company and carrying out software BEKU on a hot plate for 100 degree-Cx 120 seconds, resist thickness was measured by the nano spec. M210 (trade name: optical thickness measurement equipment).

(3) the optimal light exposure Eop --- spin-dry was performed after having performed paddle development for [23 degree-Cx] 150 seconds, using 2.38% water solution of tetramethylammonium hydroxide (TMAH) as a developer after changing the exposure time and exposing it by i line (365nm) aligner NSR[by NIKON CORP.]-1755i7A (numerical-aperture NA=0.50 of a lens), and carrying out a pure-water rinse.

Subsequently, exposure energy when forming the 10-micrometer line and the tooth-space pattern in the width of face of the ratio of 1:1 was defined as the optimal light exposure Eop (sensibility) with the electron microscope (S-4100) by Hitachi, Ltd., and it asked for it with it.

(4) The separation resolution in the optimal light exposure Eop in the resolution above (3) was shown.

(5) The resist film on the silicon wafer by which heat-resistant patterning formation

was carried out was further heated for 5 minutes at 130 degrees C on the hot plate, and it judged by whether it is held even after the pattern configuration of a 10-micrometer line and a tooth space heating.

[0029] [Synthetic example] 130g [of novolak resin of the weight average molecular weight 5,700 which uses 50 mol % of p-cresol and m-cresol 50 mol % as a raw material], and 1,2-naphthoquinone-2-diazido-5-sulfonyl chloride 14.1g, and 1,4-dioxane 650g were taught to 3 opening flask possessing an agitator, a capacitor, and a thermometer, and it dissolved in it. Triethylamine 5.6g was dropped at this solution at the room temperature. It agitated at the room temperature after dropping termination for 2 hours, and subsequently to the inside of 0.1-N hydrochloric-acid water solution of a large quantity the reaction solution was thrown in, and depositing resin was collected. The collected resin was dried with the reduced-pressure-drying machine, and the photopolymer (A) made into the 135g object was obtained.

[0030] [Example 1] Novolak resin (A)100g which was obtained in the above-mentioned synthetic example and by which 1,2-naphthoquinone-2-diazido-5-sulfonyl esterification was carried out selectively, 3.0g of compounds shown by said C-34 as a dissolution accelerator, and fluorochemical surfactant FURORINATO FC-430 (Sumitomo 3M make) 0.03g were dissolved in ethyllactate 150g. The positive-resist constituent which filters this solution with a 0.5-micrometer filter, and is made into the object was obtained. The spin coat of the obtained constituent was carried out on the silicon wafer, it prebaked in 100 degree-Cx 120 seconds on the hot plate after that, and the coat of 6.0 micrometers of thickness was formed. This was exposed in i line stepper NSR-1755i7A (NIKON CORP. make), and negatives were developed in 2.38% of tetramethylammonium hydroxide water solution. The light exposure at this time was 620 mJ/cm², and it was possible to have formed a 1.5-micrometer stripe pattern.

[0031] [Examples 2-5 and examples 1 and 2 of a comparison] The spin coat of the positive-resist constituent which blended novolak resin (A), various dissolution accelerators, the fluorochemical surfactant, and the solvent like the above-mentioned example 1, and was obtained was carried out on the silicon wafer by the same approach as an example 1, and exposure and development were performed. The result of the above-mentioned example is shown in a table 1, and the result of the example of a comparison is shown in a table 2.

[0032]

[A table 1]

実施例	1,2-キノンジ アジド化合物		溶解促進剤		溶 剤*		最適露 光量 E _{op} (mJ/cm ²)	解像度 (μ m)	パター ン形状	耐熱性
	タイプ	添加量 (部)	タイプ	添加量 (部)	種 類	添加量 (部)				
1	(A)	100	C-34	3	EL	150	620	1.5	良好	○
2	(A)	100	C-3	3	EL	150	620	1.5	良好	○
3	(A)	100	C-16	3	ECA	150	630	1.5	良好	○
4	(A)	100	C-29	3	PGMEA	150	640	1.5	良好	○
5	(A)	100	C-34	6	EL	150	440	1.5	良好	○

* ECA : エチルセロソルブアセテート
 EL : エチルラクテート
 PGMEA: プロピレングリコールモノメチルエーテルアセテート

[0033]

[A table 2]

比較例	1,2-キノンジ アジド化合物		溶解促進剤		溶 剤*		最適露 光量 E _{op} (mJ/cm ²)	解像度 (μ m)	パター ン形状	耐熱性
	タイプ	添加量 (部)	タイプ	添加量 (部)	種 類	添加量 (部)				
1	(A)	100	C-34	0.3	EL	150	700	2.0	良好	○
2	(A)	100	C-34	12.5	EL	150	320	1.5	マイクロ グループ の発生	○

* EL : エチルラクテート

[Translation done.]